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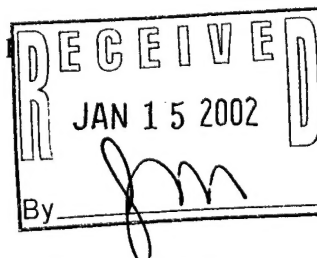
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13. ABSTRACT (Maximum 200 words)  We are studying ionic and molecular ionic compounds through a joint theoretical and experimental effort to find materials that will be microwave-active or have some related property, such as ferroelectricity or nonlinear optics. Our theoretical work involves <i>ab initio</i> molecular dynamics calculations based on pair potentials from one of two sources: the Gordon-Kim formalism or the recently developed self-consistent atomic deformation (SCAD) method. We have applied the latter method to several systems (including alkali and alkaline earth halides) to determine values of cell constants, Born charges, dielectric constants, and elastic moduli in order to gauge its efficacy for evaluating other systems not yet examined experimentally. Our results to date indicate the SCAD method produces accurate physical parameters. We are also using thin-film techniques to fabricate metastable materials predicted by the theoretical calculations to have useful or interesting properties.					
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## Final Progress Report

### Statement of the problem studied:

In order to thoroughly examine systems that hold high potential for revealing materials that are active in the microwave spectral region or that are ferroelectric, we sought to carry out a comprehensive theoretical investigation of solid solutions of ionic and molecular ionic materials in order to identify materials with the desired properties. Our goals were then to prepare and test the selected materials.

The specific objectives of this project were:

1. To conduct a comprehensive theoretical investigation of alkali nitrates, alkali nitrites, and fluoroperovskites whose structures have been experimentally determined. Molecular dynamics simulations were to be carried out to identify compounds with potential activity in the microwave spectra region. These simulations to involve construction of *a priori* electronic pair potentials which are then cast into a set of dynamical equations; these equations are examined for discontinuities which mark the phase transitions of interest.
2. To fabricate compounds predicted to have interesting properties and perform experimental characterizations of them. Equipment to accomplish these studies include high-temperature ovens (including a fluoridation oven), a Czochralski/Bridgman crystal growth apparatus, an X-ray powder diffractometer (XRD), differential thermal analyzer (DTA), differential scanning calorimeter (DSC), and thermogravimetric analyzer (TGA). Microwave activity will be studied through reflectivity and permittivity measurements at Army Research Laboratories, Aberdeen, Maryland, with whom we have a collaborative agreement.
3. To determine the theoretical and experimental effects of ionic substitution in those cases where useful characteristics may be enhanced by such a replacement.
4. To analyze the data generated from these materials to better understand the mechanisms which determine a compound's structure and phase transitions and its dielectric constants.

### Summary of the most important results:

We have completed a thorough, computational study of the electronic, structural, and vibrational properties of more than 20 ionic and molecular ionic materials using potentials derived from the self-consistent atomic deformation method (SCAD). This work is an extension of the same technique that we applied to calculating polarization and related properties of selected pnictides, chalcides, and halides. Results for oxide-based perovskites have been especially encouraging and demonstrate that the SCAD technique can be applied to systems that have previously proven to be too intractable to model. We have found that calculations that derive from SCAD (which treats the ions as non-spherical) provides better agreement with experiment than do those derived from Gordon-Kim methods (which treat the ions as rigid spheres). This is particularly so in calculating lattice parameters and dielectric constants, parameters that are particularly important when evaluating a material for ferroelectricity as well as for stabilizing it as a thin-film should the material be metastable.

One such material that SCAD-derived calculations have shown to be ferroelectric is NaCaF<sub>3</sub>. Potentials derived with SCAD were first applied to NaF and CaF<sub>2</sub> in order to calculate the lattice parameter, Born effective charge, elastic modulus, and energy gap for each. These quantities all compared well with the experimental values, which gave us additional confidence in the use of SCAD-derived potentials for calculating physical properties of materials not yet synthesized, such as NaCaF<sub>3</sub>. This material had previously been examined by Gordon–Kim techniques, which had predicted it to be both ferroelectric and metastable. The SCAD model also predicted it to be ferroelectric, with a LiNbO<sub>3</sub>-type structure with cell parameters  $a = 5.72 \text{ \AA}$  and  $c = 15.18 \text{ \AA}$ , a polarization of  $27 \mu\text{C}/\text{cm}^2$  (with the polarization along the  $c$ -axis), and a band gap of 9.2 eV. These values are similar to those calculated from the Gordon–Kim model. The band-gap calculation is an underestimate of the true band gap, based on other fluoride materials examined. Based on the calculations for NaF and CaF<sub>2</sub>, the band gap for NaCaF<sub>3</sub> should be  $\sim 12 \text{ eV}$ . The large band gap suggests that the material would be useful for second harmonic generation (SHG) because the large band gap means an absorption edge farther into the UV than is possible with oxide materials.

Total energy calculations of NaCaF<sub>3</sub> from the SCAD model indicate that it is degenerate with its binary components, viz., NaF and CaF<sub>2</sub>. The fact that the binary components do not react to form the ternary compound using standard techniques implies that its true total energy is greater than that calculated, or the energies associated with ferroelectric domain formation are significant, or both. Efforts are on-going to stabilize the material on a lattice-matched substrate as a thin-film.

Preliminary theoretical work has been done on the metastable material NaSrF<sub>3</sub>. Gordon–Kim calculations predict it to be a ferroelectric with a transition temperature of  $\sim 800 \text{ K}$  and a tetragonal crystal structure. SCAD modeling is in progress in order to provide additional confirmation for these initial results. If the SCAD results are encouraging, efforts to make it by thin-film techniques will be commenced.

A study of the electronic structure and the linear and nonlinear optical properties of KNbO<sub>3</sub> was conducted using a first-principles local-density approximation. Calculated results of the refractive indices and second-harmonic generation coefficients agree well with experiments, which gives us confidence in the calculated results for other properties. From the nonlinear susceptibility, the primary contribution to the nonlinear behavior is the hybridization of the oxygen 2p and niobium 4d electronic states.

Structural transitions were also calculated for alkaline-earth silicates, alkali perchlorates, alkali nitrates, silver nitrate, thallium azide, and calcium carbonate.

### **Listing of all publications and technical reports:**

#### **(a) Papers published in peer-reviewed journals**

1. J. Liu, C. Duan, W. N. Mei, R. W. Smith, and J. R. Hardy, "Polymorphous transitions in alkaline-earth silicates," *Journal of Chemical Physics*, in press.
2. J. Liu, C. Duan, W. N. Mei, R. W. Smith, and J. R. Hardy, "Order-disorder structural phase transitions in alkali perchlorates," *Journal of Solid State Chemistry*, in press.

3. J. Liu, C. Duan, M. M. Ossowski, W. N. Mei, R. W. Smith, and J. R. Hardy, "Molecular dynamics simulation of phase transition in  $\text{AgNO}_3$ ," *Journal of Physics and Chemistry of Solids*, in press.
4. J. Liu, C. Duan, M. M. Ossowski, W. N. Mei, R. W. Smith, and J. R. Hardy, "High temperature phase transition in  $\text{TiN}_3$ ," *Materials Research Bulletin* **36**, 2035-2041 (2001).
5. J. Liu, C. Duan, M. M. Ossowski, W. N. Mei, R. W. Smith, and J. R. Hardy, "Simulation of structural phase transitions in  $\text{NaNO}_3$  and  $\text{CaCO}_3$ ," *Physics and Chemistry of Minerals* **28**, 586-590 (2001).
6. J. Liu, C. Duan, M. M. Ossowski, W. N. Mei, R. W. Smith, and J. R. Hardy, "Molecular dynamics simulation of structural phase transitions in  $\text{RbNO}_3$  and  $\text{CsNO}_3$ ," *Journal of Solid State Chemistry* **160**, 222-229 (2001).
7. C. Duan, W. N. Mei, J. Liu, and J. R. Hardy, "First-principles study on the optical properties of  $\text{KNbO}_3$ ," *Journal of Physics: Condensed Matter* **13**, 1-7 (2001).
8. C. Duan, W. N. Mei, R. W. Smith, J. Liu, M. M. Ossowski, and J. R. Hardy, "Order-disorder phase transitions in  $\text{KNO}_2$ ,  $\text{CsNO}_2$ , and  $\text{TiNO}_2$  Crystals: A molecular dynamics study," *Physical Review B* **63**, 144105-1-144105-6 (2001).
9. M. M. Ossowski, J. R. Hardy, and R. W. Smith, "Molecular dynamics study of phase transitions in alkali thiocyanates," *Physical Review B* **62**, 3136-3141 (2000).
10. W. N. Mei, L. L. Boyer, M. J. Mehl, M. M. Ossowski, and H. T. Stokes, "Calculation of electronic, structural and vibrational properties in alkali halides using a density functional method with localized densities," *Physical Review B* **61**, 11425-11431 (2000).
11. R. W. Smith, W. N. Mei, J. W. Flocken, M. J. Dudik, and J. R. Hardy, "Polymorphic phase transitions in mixed alkali magnesium fluoride solid solutions," *Materials Research Bulletin* **35**, 341-349 (2000).
12. M. M. Ossowski, J. R. Hardy, and R. W. Smith, "Molecular dynamics study of phase transitions in alkali azides," *Physical Review B* **60**, 15094-15099 (1999).

(b) Papers published in conference proceedings

1. L. L. Boyer, M. J. Mehl, W. N. Mei, C. Duan, J. W. Flocken, R. A. Guenther, J. R. Hardy, H. T. Stokes, P. J. Edwardson, "Predicted properties of  $\text{NaCaF}_3$ ," *Fundamentals of Ferroelectrics 2000, AIP Conference Proceedings* **535**, R. E. Cohen, Ed., 364-371 (2000).
2. J. Liu, M. M. Ossowski, and J. R. Hardy, "Simulation of structural transformation in aragonite  $\text{CaCO}_3$ ," *Fundamentals of Ferroelectrics 2000, AIP Conference Proceedings* **535**, R. E. Cohen, Ed., 338-343 (2000).
3. M. M. Ossowski, J. R. Hardy, and R. W. Smith, "Structural transitions in  $\text{NaCN}$  and  $\text{KCN}$ ," *Fundamentals of Ferroelectrics 2000, AIP Conference Proceedings* **535**, R. E. Cohen, Ed., 332-337 (2000).

(c) Papers presented at meetings but not published in conference proceedings

none

(d) Manuscripts submitted, but not published

none

(e) Technical reports submitted to ARO

none

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**Report of inventions:**

"Ferroelectric Materials with Chemical Formula  $A(1-x)B(x)C(1-y)D(y)F_3$  and Fabrication Thereof," R. W. Smith and J. S. Horwitz, U.S. Patent Office, submitted 20 September 1999.